Preparation of Tetrachlorophosphonium Tetrachlorochromate(III). (i) Weber's Method.[6] Phosphorus pentachloride (2.5 g) was heated with chromium(VI) dioxide dichloride (0.25 cm^3) in a vacuum-sealed Carius tube at 140 °C for 4 h. The resultant blue-purple powder was dried in vacuo. Anal. Calcd for Cl_8CrP: Cl, 77.37; Cr, 14.18; P, 8.45. Found: Cl, 77.0; Cr, 14.0; P, 8.58.

(ii) Groeneveld's Method.[2] Phosphorus trichloride (4.8 cm^3) was added slowly to a solution of chromium(VI) dioxide dichloride (3 cm^3) in phosphorus oxide trichloride (75 cm^3). A solution of phosphorus pentachloride (7.5 g) in phosphorus oxide trichloride (30 cm^3) was then added to the purple solution, and the resultant violet powder was filtered off in vacuo, washed with phosphorus oxide trichloride (75 cm^3), and dried in vacuo. Anal. Calcd for Cl_8CrP: Cr, 14.18; P, 8.45. Calcd for $[Cl_8CrP + 7\%\ POCl_3]$: Cr, 13.78; P, 8.78. Found by Groeneveld:[2] Cr, 13.7; P, 8.7.

Acknowledgment. We would like to express our gratitude to the Central Electricity Generating Board for financing this work and for awarding a research fellowship at St. Catherine's College (to K.R.S.) and a research studentship (to V.H.T.).

Registry No. $(PCl_4)[CrOCl_4]$, 65045-58-1; $(PCl_4)[CrCl_4]$, 13859-46-6; PCl_5, 10026-13-8; CrO_2Cl_2, 7791-14-2.

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The Pfeiffer Effect with a Dissymmetric Metal Complex as an Environment Substance

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Received July 8, 1977

In our previous paper,[1] it was reported that the chiral equilibrium between Δ- and Λ-tris(acetylacetonato)cobaltate(II) (abbreviated as Δ- and Λ-$[Co(acac)_3]^-$) is displaced in favor of the former enantiomer upon the addition of Λ-tris(1,10-phenanthroline)cobalt(III) (abbreviated as Λ-$[Co(phen)_3]^{3+}$) in aqueous solutions. This system is, we believe, the first Pfeiffer-active system[2] in which a dissymmetric metal complex serves as a chiral environment substance. We present here another Pfeiffer-active system with Λ-$[Co(phen)_3]^{3+}$ as an environment substance.

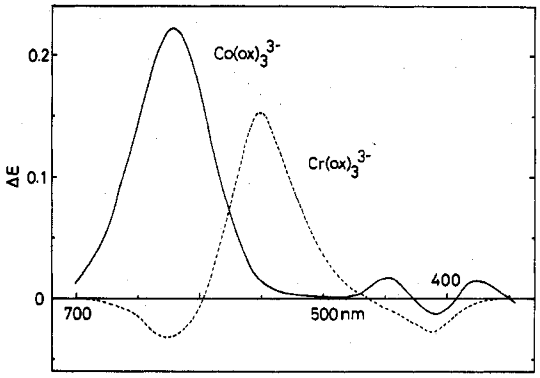

Figure 1. CD spectra for the $[Cr(ox)_3]^{3-}$ (4.39 mM)–Λ-$[Co(phen)_3]^{3+}$ (13.6 mM) and the $[Co(ox)_3]^{3-}$ (6.44 mM)–Λ-$[Co(phen)_3]^{3+}$ (10.2 mM) systems to each of which 10 mL of dioxane was added.

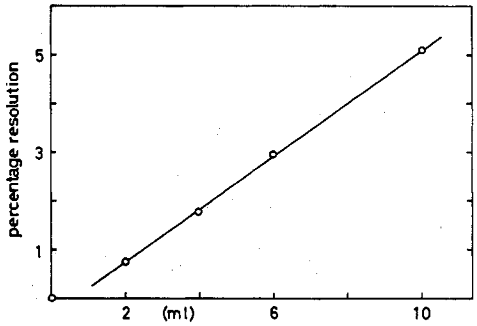

Figure 2. Influence of added dioxane on the percentage resolution for the $[Cr(ox)_3]^{3-}$ (4.39 mM)–Λ-$[Co(phen)_3]^{3+}$ (13.6 mM) system.

Experimental Section

Racemic $K_3[Cr(ox)_3]\cdot 3H_2O$ and $K_3[Co(ox)_3]\cdot 3H_2O$ (ox = oxalate anion) were prepared by standard methods,[3] and Λ-$[Co(phen)_3](ClO_4)_3\cdot 3H_2O$ resolved by a usual method[4] was converted to the chloride form by treating with a Dowex 1X8 anion-exchange resin in Cl^- form. Sample solutions were prepared by mixing aqueous stock solutions of $K_3[Cr(ox)_3]$ or $K_3[Co(ox)_3]$ with those of Λ-$[Co(phen)_3]Cl_3$ in volumetric flasks (25 mL) to which varying amounts (up to 10 mL) of dioxane (reagent grade) were added. These solutions were kept standing in the dark for 1 day to attain the chiral equilibrium[5] and then were poured into a cation-exchange column (SP-Sephadex C-25 in Na^+ form) to remove Λ-$[Co(phen)_3]^{3+}$. During the ion-exchange process, the column was cooled with ice water to depress the racemization of $[Cr(ox)_3]^{3-}$ or $[Co(ox)_3]^{3-}$. Great care was taken to ensure that no precipitate was formed in the sample solutions as well as in the cation-exchange column, for Λ-$[Co(phen)_3]^{3+}$ precipitates preferentially with Λ-$[Cr(ox)_3]^{3-}$ or Λ-$[Co(ox)_3]^{3-}$ if a large amount of dioxane is added. The absorption (AB) and circular dichroism (CD) spectra were recorded for the effluents from the column as quickly as possible on a Shimadzu UV-200 and a Jasco J-40CS spectrometer, respectively.

Results and Discussion

The CD spectra (Figure 1) obtained for the $[Cr(ox)_3]^{3-}$ and $[Co(ox)_3]^{3-}$ systems clearly indicate that Λ enantiomer[6] is enriched in both systems when Λ-$[Co(phen)_3]^{3+}$ is employed as an environment, though Δ enantiomer is enriched in the $[Co(acac)_3]^-$–Λ-$[Co(phen)_3]^{3+}$ system.[1] This means that the Pfeiffer effect does not always work as a reliable means for the determination of the absolute configuration of labile metal complexes, as was pointed out earlier.[7]

By comparing the CD intensities at 552 nm,[6a] the percentage resolution was estimated and is plotted in Figure 2 as a function of the amount of added dioxane for the $[Cr(ox)_3]^{3-}$ system. It is seen that the addition of dioxane is quite favorable to this Pfeiffer system;[8] no optical activity is detected under our experimental conditions unless dioxane is added. Though it is not known at present why added dioxane enhances the Pfeiffer effect so greatly, an accompanying decrease in di-

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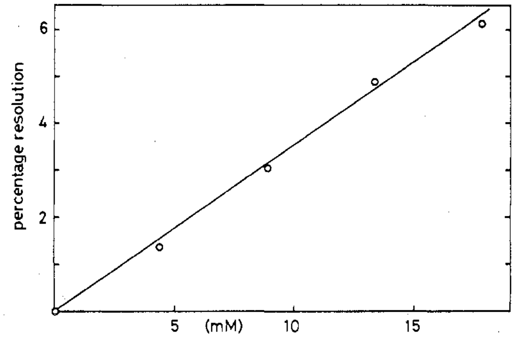

Figure 3. Dependence of the percentage resolution on the concentration of Λ-$[\mathrm{Co(phen)_3}]^{3+}$ for the $[\mathrm{Cr(ox)_3}]^{3-}$ (7.54 mM) system.

electric constant of the medium will lead to enhanced electrostatic association of $[\mathrm{Cr(ox)_3}]^{3-}$ or $[\mathrm{Co(ox)_3}]^{3-}$ with Λ-$[\mathrm{Co(phen)_3}]^{3+}$.

In Figure 3 is plotted the percentage resolution for the $[\mathrm{Cr(ox)_3}]^{3-}$ system as a function of the amount of added Λ-$[\mathrm{Co(phen)_3}]^{3+}$, the amounts of the racemic complex and added dioxane being kept constant (7.54 mM and 10 mL/25 mL of solution, respectively). It is seen that the percentage resolution is enhanced almost linearly with the amount of the chiral environment substance, as is usually the case.[2]

There have already appeared two Pfeiffer-active systems with a metal complex as an environment in the literature. One is the $[\mathrm{Zn(phen)_3}]^{2+}$–$\Lambda$-$[\mathrm{Co(en)_3}]^{3+}$ system in water.[9] However, strong electrostatic repulsion between the two cationic complexes will prohibit their favorable interaction. Then, the $[\mathrm{Ni(phen)_3}]^{2+}$–$\Lambda$-$[\mathrm{Co(en)_3}]^{3+}$ system was examined in place of the zinc complex system. An aqueous mixture of the two complexes kept standing for 2 weeks[10] was subjected to a column chromatography (SP-Sephadex C-25 in $\mathrm{Na^+}$ form) with aqueous NaCl (0.1 M) as an eluent. Only the first band corresponding to the nickel complex was collected, but it was found CD inactive. This result is consistent with the earlier finding[11] that no difference is observed in the racemization rates of Δ- and Λ-$[\mathrm{Ni(phen)_3}]^{2+}$ in the presence of Λ-$[\mathrm{Co(en)_3}]^{3+}$. Therefore, the $[\mathrm{Zn(phen)_3}]^{2+}$–$\Lambda$-$[\mathrm{Co(en)_3}]^{3+}$ system is supposed to be also Pfeiffer-inactive.[12]

The other is the $[\mathrm{Ni(acac)_3}]^{-}$–$\Lambda$-$[\mathrm{Co(en)_3}]^{3+}$ system in water, which was recently proposed to be Pfeiffer-active by Pollock et al.[13] However, the $[\mathrm{Co(acac)_3}]^{-}$–$\Lambda$-$[\mathrm{Co(en)_3}]^{3+}$ system similar to the above system was found Pfeiffer-inactive in our previous study.[1] Since they could not detect directly the CD spectrum due to $[\mathrm{Ni(acac)_3}]^{-}$, their proposal is open to question. On the other hand, the $[\mathrm{Co(acac)_3}]^{-}$–$\Lambda$-$[\mathrm{Co(phen)_3}]^{3+}$ and the present $[\mathrm{Cr(ox)_3}]^{3-}$– or $[\mathrm{Co(ox)_3}]^{3-}$–Λ-$[\mathrm{Co(phen)_3}]^{3+}$ systems are undoubtedly Pfeiffer-active systems with a dissymmetric metal complex as an environment substance.

Registry No. $[\mathrm{Cr(ox)_3}]^{3-}$, 15054-01-0; $[\mathrm{Co(ox)_3}]^{3-}$, 15053-34-6; Λ-$[\mathrm{Co(phen)_3}]^{3+}$, 24501-38-0; dioxane, 123-91-1.

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Protonation of the Pentacyanoaquaferrate(II) Ion, $\mathrm{Fe(CN)_5OH_2{}^{3-}(aq)}$

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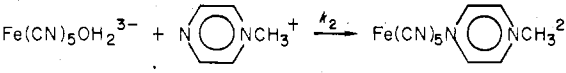
Received June 28, 1977

Recently, a number of studies involving kinetics of complexation by the pentacyanoaquaferrate(II) ion, $\mathrm{Fe(CN)_5OH_2{}^{3-}(aq)}$, have been made.[1-6] Like other complexes involving the pentacyanoferrate(II) moiety,[7] the aqua complex is expected to behave as a weak base, protonatable at cyanide. However, the pK_a of its conjugate acid and also the substitution reactivity of that species have remained unknown. Because the aqueous pentacyanoaquaferrate(II) ion is a reactant used in a new class of electron-transfer "precursor" intermediates,[1c,5] a knowledge of its properties in the protonated form is especially important.

Complications introduced by formation and protonation of polynuclear species, e.g., $\mathrm{Fe_2CN_{10}{}^{6-}(aq)}$,[6,8] make direct measurement of the pK_a by pH titration extremely difficult. Therefore, we have studied the kinetics of the aqueous substitution reaction, eq 1, within the pH range 1.0–7.5 at 25 °C,



(1)

μ = 0.1 M ($\mathrm{LiClO_4}$). The complexing agent *N*-methylpyrazinium ion ($\mathrm{Me(pyr)^+}$) neither gains nor loses a proton within this pH interval. The results show that the pK_a of $\mathrm{HFe(CN)_5OH_2{}^{2-}}$ is 2.63 ± 0.12, under the experimental conditions. A striking diminution in substitution reactivity is seen in the protonated form.

Experimental Section

Materials and Methods. Doubly distilled water containing appropriate buffers, reagent grade perchloric acid, and lithium perchlorate were the reaction medium. pH values were measured using an Orion 801 pH meter.

N-Methylpyrazinium iodide was prepared by methylation of pyrazine.[9] Anal. Calcd for $\mathrm{C_5H_7N_2I}$: C, 27.05; H, 3.18; N, 12.62. Found: C, 26,86; H, 3.27; N, 12.61.[10] In the kinetics experiments, control of pH in the reaction mixture was accomplished by adding acetate or phosphate buffers, or perchloric acid, to the Me(pyr) solutions.

$\mathrm{Na_3[Fe(CN)_5NH_3]\cdot 3H_2O}$ was prepared as described previously,[11] washed with methanol, and stored in vacuo in the dark. Anal. Calcd for $\mathrm{Na_3FeC_5H_9N_6O_3}$: C, 18.24; H, 2.78; N, 25.78. Found: C, 18.18; H, 2.84; N, 25.71. For the kinetics studies, solutions of $\mathrm{Fe(CN)_5OH_2{}^{3-}}$ were produced by dissolving ca. 1.5×10^{-5} mol of the above salt in 250 mL of water at pH ~10 (unbuffered). A 5.00-mL sample of this solution was added immediately to 45.00 mL of dilute lithium perchlorate solution, also at pH ~10, for use in the Durrum D-110 stopped-flow instrument. Syringe-transfer techniques, $\mathrm{N_2}$ blanketing gas, and low light levels were employed to minimize the decomposition of the reactant iron(II) complex. Experiments were performed within the shortest possible time after dissolving the pentacyanoferrate(II) salt. Because of these precautions, little evidence was found of the slowly reacting polynuclear iron(II) cyanides that have been described previously.[1a,5,6,8] Slow, secondary absorbance increases could be